

[54] GAS EXTRACTION

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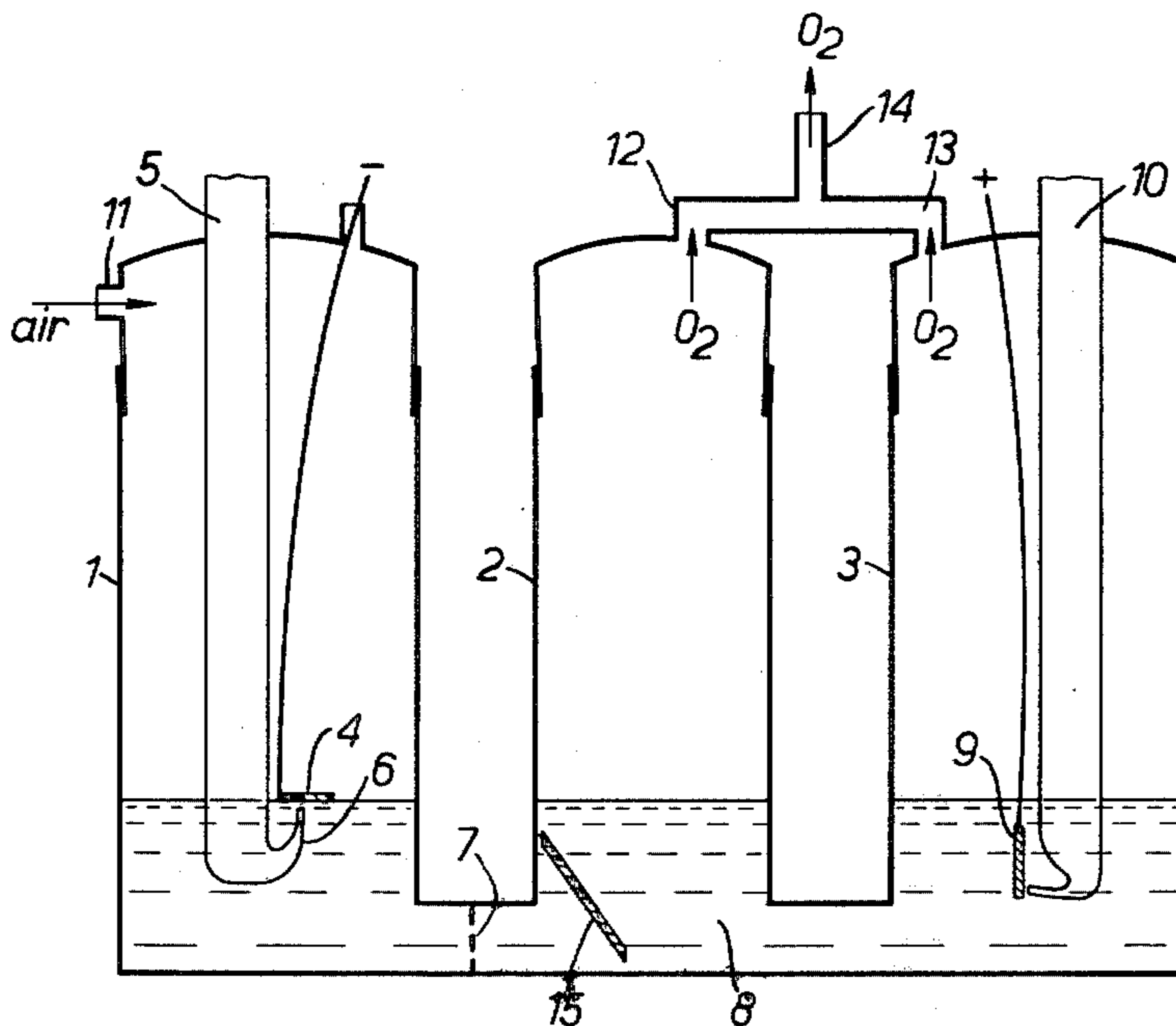
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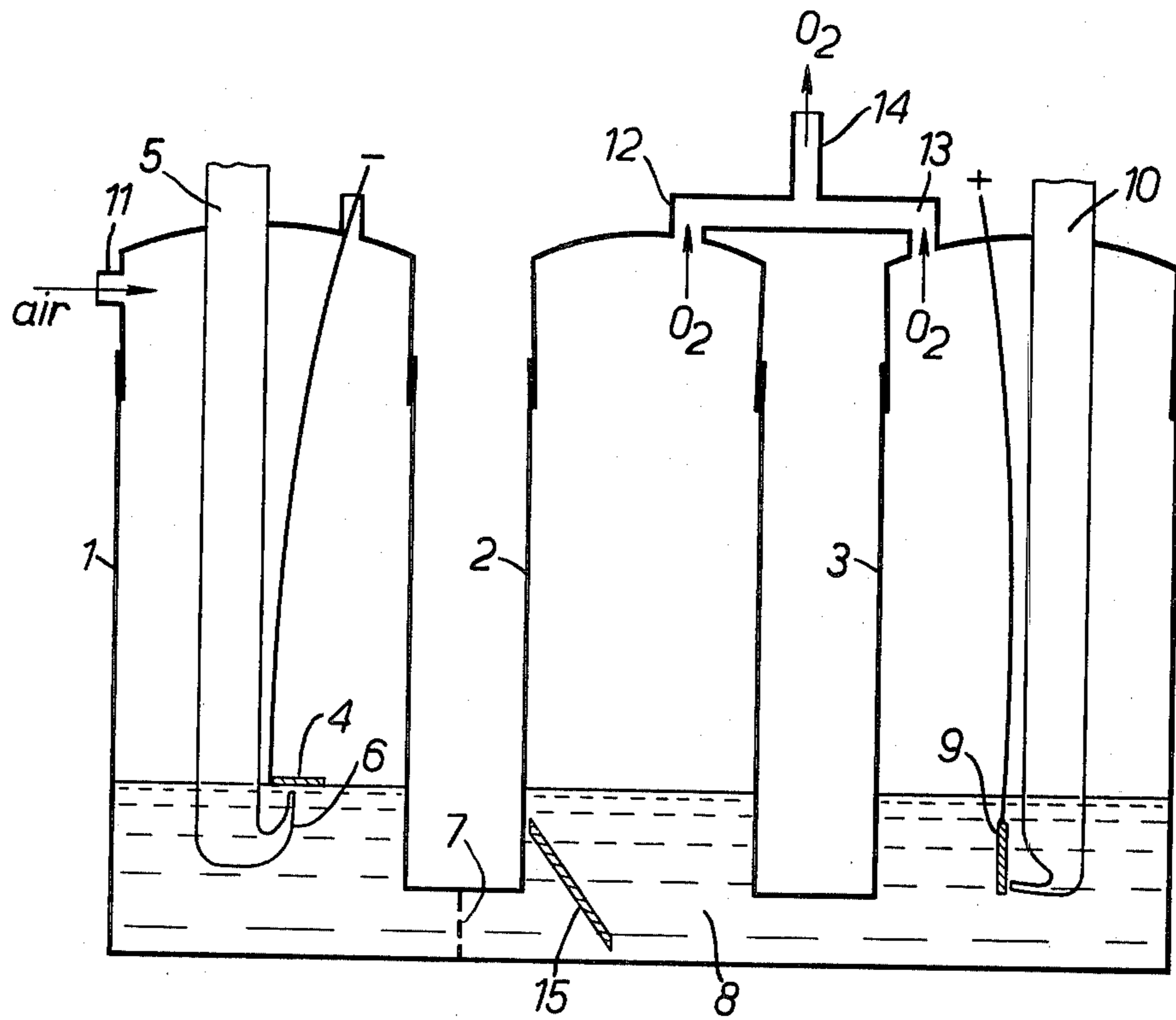
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[57] ABSTRACT

An electrochemical cell used to separate gas from a gaseous mixture by reduction of said gas at the cathode and regeneration of said gas at the anode is characterized in that one or more substances formed during the cathodic reduction and/or the anodic regeneration is chemically converted, preferably by catalytic decomposition, to produce further quantities of said gas, the gas formed by both the anodic regeneration and the chemical conversion being recovered as the product. In an especially preferred embodiment a plurality of said cells are used in apparatus for extracting oxygen from the air by using a cathode comprising high surface area graphite powder which reduces oxygen to produce peroxy ions, each cell being further provided, externally of the cathode compartment, with means for catalytically decomposing the peroxy ions produced, suitable catalysts being CoFe_2O_4 or NiCo_2O_4 .

18 Claims, 1 Drawing Figure





GAS EXTRACTION

This is a division of application Ser. No. 137,114, filed as PCT GB 79/00060, Apr. 11, 1979, published as WO 79/00933, Nov. 15, 1979 § 102(e) date on Nov. 5, 1979, now U.S. Pat. No. 4,300,987.

This invention relates to the extraction of gases from gaseous mixtures and, more especially, to the extraction of oxygen from ambient air.

Portable oxygen providing equipment is finding increasing applications in military field hospitals, in the village clinics of developing countries, in oxy-acetylene welding and in high altitude fighter aircraft. Besides oxygen cylinders, such equipment comprises two basic types of oxygen generator; (a) chemical generators, and (b) electrochemical generators, which either electrolyse water or else extract oxygen from the air by using an oxygen reduction cathode coupled to an oxygen evolution anode.

Chemical generators employ expensive chemicals and, to date, the most common method used to generate oxygen has been the electrolysis of water. However, the high overvoltage at the anode necessitates an operating voltage of about 2.2 volts at 100 mA/cm² and the production of hydrogen as a by-product, apart from increasing the power consumption, is a potential hazard. Quite recently, therefore, there has been developed a more efficient electrochemical method in which a polytetrafluoroethylene (PTFE) bonded platinum black cathode is used to reduce oxygen in the ambient air to form hydroxyl ions in accordance with the following equation:



The hydroxyl ions diffuse through a suitable membrane, for example, a woven asbestos or glass fibre mat, to an oxygen evolution anode, usually a platinum electrode. The working voltage of this cell, taking into account the unavoidable heat losses, is about 1.3 to 1.4 volts at 100 mA/cm², which is significantly lower than the corresponding value for an electrolysis cell. However, the capital and running costs involved are still relatively high and the use of this type of oxygen extractor has been limited to specialised applications.

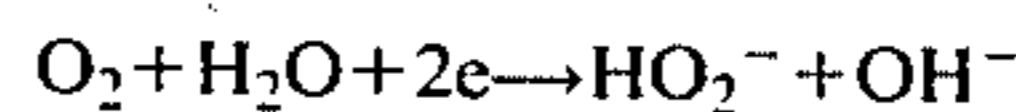
The present invention is based on our surprising observation that the efficiency of such electrochemical gas extraction and regeneration methods can be improved significantly in certain applications by employing an additional chemical step in which one or more substances formed in the electrochemical reaction is itself converted to the desired gaseous product, preferably by catalytic decomposition.

Accordingly, the present invention provides a method in which an electrochemical cell is used to separate a gas from a gaseous mixture by reduction of said gas at the cathode and regeneration of said gas at the anode, characterised in that one or more substances formed in the cathodic reduction and/or the anodic regeneration is chemically converted to produce said gas and in that the gas formed by both the anodic regeneration and the chemical conversion is recovered as the product. The present invention also provides apparatus for carrying out such a method.

In its broad aspect the present invention may be applied to the extraction of any gas from a gaseous mixture, provided that said gas may selectively be cathodically reduced and anodically regenerated by electrochemical reactions which produce a substance which can be chemically converted to said gas, preferably by

catalytic decomposition. However, it will be appreciated from the foregoing remarks that the invention is especially applicable to the extraction of oxygen from ambient air and, for convenience, it will now be described in more detail with reference to such an application.

It is known that the reduction of oxygen on certain electrodes, especially graphite and carbon, is a two electron process obeying the equation



This means that when such electrodes are used in a fuel cell, they are not so efficient as electrodes which directly reduce oxygen to hydroxyl ions via a four electron process. It has, therefore, been proposed to add peroxide-decomposition catalysts to a carbon cathode in a fuel cell so that the peroxy ion is decomposed to yield oxygen for recycling, thus leading to a higher efficiency. In accordance with the present invention; however, the catalytic decomposition of the peroxy ion is used in an oxygen generator to provide an additional supply of oxygen as product.

In an especially preferred form of the present invention, therefore, there is provided an oxygen extraction apparatus comprising at least one cell which is provided with a cathode for the reduction of oxygen by an electrochemical reaction which produces peroxy ions and an anode which will regenerate oxygen characterised in that said cell is further provided, externally of the cathode compartment, with means for the catalytic decomposition of hydrogen peroxy ions.

It will be appreciated that such apparatus will also be provided with means for the supply of ambient air at a suitable rate and also with means for collecting the oxygen produced by the electrochemical and chemical reactions. In practice the apparatus will typically comprise a plurality of such cells, for example from 10 to 20, and may advantageously be built to a modular design for ease of replacement and repair of the cells. It will, in any case, be appreciated that the design of the apparatus will depend upon the particular application and, especially, upon the desired rate of production of oxygen.

Suitable physical constructions for the cell will be apparent to those conversant with fuel cell technology. For example it will, in general, be appropriate to provide means such as a porous screen made, for example, from asbestos or glass to separate the cathode compartment from the remainder of the cell in order to prevent back diffusion of oxygen bubbles to the cathode compartment and to prevent diffusion of air bubbles into the product stream. If the cell is compact in nature it may be necessary to provide means such, for example, as a net made from a plastics or other insulating material, to ensure that there is no electrical contact between the anode and the catalytic means.

Other constructional features which may prove advantageous or necessary in certain applications include means for removing carbon dioxide, means for removing electrolyte, e.g. potassium hydroxide, entrained in the oxygen product stream and means for controlling the oxygen content of the final outlet gas by admixture of the oxygen product stream with exhaust gas from the cathode compartment; this is essential in some medical applications. It will, in addition, in general be necessary to provide adequate means for controlling the voltage, current density, temperature and operating pressure of

the cell and for monitoring the overall heat and mass balance of the apparatus.

In this preferred application of the present invention it is necessary for the cathode to reduce oxygen by an electrochemical route which produces peroxy ions, usually together with hydroxyl ions (generally via the two electron process described above or a near stoichiometric variation thereof) but which is made from a material which does not possess significant peroxide decomposition activity. For example, cathode materials such as fuel cell grade platinum black produce peroxy ions but, because they have a relatively high peroxide decomposition activity, will not, in general, be suitable for use in the present invention because the peroxide ion will be decomposed in the cathode compartment and the oxygen so produced cannot be collected with the oxygen produced at the anode.

In general it is preferred to use a high surface area graphite powder which has been found to possess a very high activity for oxygen reduction in alkaline solution. A suitable graphite powder having a surface area in the range of 500 to 600 m²/g may be prepared by vacuum grinding of graphite in a vibrating ball mill; the cathode may be prepared from the graphite powder by bonding with PTFE. However, it will be appreciated that other materials may be suitable for the cathode in certain applications.

The main criterion for the oxygen evolution anode is that it should operate at a low oxygen overvoltage. Thus certain anodes such as PTFE-bonded platinum black and nickel screens will not, in general, be suitable for use in the present invention. However, amongst suitable materials there may be mentioned, for example, PTFE-bonded lithiated nickel oxide and, especially, PTFE-bonded nickel cobalt oxide (NiCo₂O₄) which has a lower redox potential than a platinum black anode.

Both the cathode and anode may, in some cases, advantageously be formed by depositing the active materials on a suitable support, such as a nickel screen.

The electrolyte itself is advantageously an aqueous solution of an alkali metal hydroxide, e.g. sodium hydroxide, or especially, potassium hydroxide, but it will be appreciated that other electrolytes may be useful in certain applications.

The essence of this preferred application of the present invention is to provide means for catalytically decomposing hydrogen peroxide (or, more correctly, the peroxy ion which it forms in the electrolyte) to produce an additional supply of oxygen for collection in the anode compartment. In this way, the effective current required for the oxygen extraction process is halved leading to a significant reduction in power consumption. In certain instances it may be appropriate to provide such means as a chemical substance in solution or dispersion in the electrolyte, but, in general, it will be preferred to provide the catalyst in the form of a solid member or, more especially, absorbed or coated on a suitable solid support. Amongst suitable materials there may be mentioned, for example, certain spinel oxides and silver which may be coated or absorbed on a graphite or carbon support. Preferred peroxide decomposition catalysts are CoFe₂O₄ and, especially, NiCo₂O₄. These materials may be brought into suitable form by bonding with PTFE, but, in general, it will be preferred to coat them on a suitable porous or perforated support, e.g. a nickel screen. It has been found that their activity is considerably greater in the latter form because the catalytic reaction can more easily occur on the surface

of the screen and because, in addition, the available surface of the screen is entirely composed of the catalyst whereas about 50% of a PTFE-bonded member is composed of PTFE particles where no catalytic reaction can occur.

Both CoFe₂O₄ and NiCo₂O₄ are relatively cheap materials which can be produced in particulate form by freeze-drying methods or by thermal decomposition or double precipitation methods.

In summary, it may be stated that the electrochemical/chemical method of oxygen extraction according to the present invention provides significant advantages in cost reduction and in other respects as compared with the conventional electrochemical oxygen extractors at present available. At operating voltages of around 1 volt and at an operating temperature of 40° C. with 5N KOH as the electrolyte the approximate power consumption of a cell constructed in accordance with the present invention is only about 2.7 to 3 kilowatt hours per 1,000 liters of oxygen produced whereas conventional extractors require about 4.4 kilowatt hours. Rough calculations indicate that if the cells of the present invention are used in an efficient manner they will be capable of producing oxygen in a relatively cheap manner and will lead to significant savings in cost in applications where oxygen cylinders are at present employed.

The following Examples illustrate the invention. The FIGURE shows diagrammatically apparatus for extracting gases from gaseous mixtures in accordance with the invention. A three compartment cell was constructed as shown in the FIGURE. It will be appreciated that the cell shown was constructed for experimental evaluation of various aspects of the present invention and is not to be considered as typical of a cell to be used commercially.

The cell generally comprises a cathode compartment 1, a catalytic decomposition compartment 2 containing a catalytic decomposer 15, and an anode compartment 3. The cathode compartment 1 was provided with a floating electrode 4 and, as shown, a Dynamic Hydrogen Reference electrode (DHE) 5 was used to monitor the potential working electrode 4, the tip of the Luggin capillary 6 of the DHE electrode 5 being positioned about 1 mm below the floating electrode 4. If desired, the cathode compartment 1 may be separated from the remainder of the cell by the provision of a No. 4 glass frit 7. 5N KOH solution was used as the electrolyte 8. A catalytic decomposer 15 was provided in compartment 2. The anode compartment 3 was provided with a working anode 9 and with a DHE electrode 10. Air was passed into cathode compartment 1 via inlet 11 and the oxygen produced in compartments 2 and 3 was collected by means of outlets 12 and 13, respectively. As shown, outlets 12 and 13 led to a further combined outlet 14.

EXAMPLE 1

In this Example a cell was used having two compartments separated by a No. 4 glass frit and provided with a 8 cm² PTFE-bonded graphite floating cathode and a 20 cm² nickel screen anode. Current was passed at the fixed densities shown using a Chemical Electronics Potentiostat (TR 40-3A). The 5N KOH electrolyte (80 ml) was thermostated at 25° C. and an air pump was used to supply air to the cathode compartment.

After 1 hour, the concentration of H₂O₂ in the electrolyte was measured by titration against standard po-

tassium permanganate solution. The self decomposition of H_2O_2 in 5N KOH under the same condition (but without passing current) was measured and found to be 0.525 g/liter of HO_2^- per hour. The numbers of runs is shown in brackets.

Table 1 shows the amounts of HO_2^- produced at different current densities and confirms that the reduction of oxygen on graphite proceeds via the two electron process.

The 74% yield of HO_2^- as compared with theoretical was mainly due to decomposition on the nickel screen anode and losses during pipetting and titration.

TABLE 1

Current mA	Theoretical gm HO_2^-	Experimental average gm HO_2^- (in 80 ml. electrolyte)	Experimental/ Theoretical %
200	0.1230	0.0917	74.55 (2)
400	0.2460	0.1866	75.85 (2)
600	0.3693	0.2675	72.40 (2)
800	0.4924	0.3575	72.6 \pm 0.02 (4)

EXAMPLE 2

Various electrode combinations were evaluated using the cell shown in the FIGURE. A Chemical Electronics Potentiometer (TR 40-3A) was used to feed a 400 mA current to the cell for 30 minutes and a gas burette was attached to outlet 14 to measure the amount of oxygen produced (except that the glass frit 7 was omitted).

The PTFE-bonded cathodes were prepared in a conventional manner, the $NiCo_2O_4$ /nickel screen catalytic decomposers and the PTFE-bonded $NiCo_2O_4$ /nickel screen anodes were prepared as follows:

(a) $NiCo_2O_4$ /nickel screen catalytic decomposers.

100 mesh nickel screen were dipped into 2M Ni/Co nitrate solution (Ni:Co=1:2) and the screens were heated in air at 400° C. for 10 hours. The formation of $NiCo_2O_4$ spinel on the surface of the screen was confirmed by X-ray powder diffraction.

(b) PTFE-bonded screen anodes. $NiCo_2O_4$ (prepared by freeze drying) was mixed with GP1-Fluon dispersion (ex ICI). The $NiCo_2O_4$:PTFE ratio was

10:3. The mixture was then painted onto a 100 mesh nickel screen and dried at 100° C. for 1 hour.

The results obtained with the various electrode and catalytic decomposer combinations are shown in Table 2.

It will be seen that the best results were obtained when operating in accordance with the present invention (cells A and B) using a PTFE-bonded graphite/screen cathode and a PTFE-bonded $NiCo_2O_4$ /nickel screen anode with a $NiCo_2O_4$ /nickel screen catalytic decomposer.

When no catalytic decomposer was employed (cell C) the power consumption was similar to that with a cell using platinum black as the cathode (cell D). Even though, in cell C, the cathodic reduction of oxygen occurred by a two electron process, the peroxide ions diffusing to the anode were not fully decomposed and when the power was switched off gassing continued slowly for a long time on the PTFE-bonded $NiCo_2O_4$ anode surface (which is not so active as the thermally decomposed $NiCo_2O_4$ /nickel screen catalytic decomposer). This suggests that when the anode is functioning electrochemically the oxygen bubbles effectively blanket a large part of its surface, making it unavailable for peroxide decomposition.

When a peroxide decomposer was placed between a platinum cathode and the $NiCo_2O_4$ anode (cell E) no improvement was noted. This is not surprising because any HO_2^- ions produced at the platinum cathode would be decomposed there, yielding oxygen for further cathodic reduction.

It will be seen that in all cases the power consumption was significantly lower than for a conventional water electrolyser (cell F) and that cell B, constructed in accordance with the present invention, gives significantly better results than the previously proposed cell (cell G) using a platinum black anode and cathode.

Finally, it will be noted that in the experimental cells A and B, not all the peroxy ions produced were decomposed. This is mainly because of the large distance between the anode and cathode and significant improvements in peroxide conversion can be obtained by decreasing the anode/cathode gap.

TABLE 2

Cell No.	Temp.	Cathode	Extraction of oxygen from air (400 mA passed through cell for 30 min)				Voltage iR free volt	Power consumption KW hr/1000 liters of O_2	
			H_2O_2 decomposer	Anode	Theoretical				Experimental ml (NTP)
					From H_2O_2 decomposition ml (NTP)	From O_2 evolution ml (NTP)			
A	25° C.	4 cm ² Teflon bonded graphite on nickel screen	4 cm ² $NiCo_2O_4$ on nickel screen	4 cm ² Teflon bonded $NiCo_2O_4$ on nickel screen	45.60	45.60	78.03 \pm 3.18 (5)	1.34	3.46
B	40° C.	4 cm ² Teflon bonded graphite on nickel screen	4 cm ² $NiCo_2O_4$ on nickel screen	4 cm ² Teflon bonded $NiCo_2O_4$ on nickel screen (O_2 evolving)	45.60	45.60	77.04 \pm 3.02 (4)	1.04	2.69
C	25° C.	4 cm ² Teflon bonded graphite on nickel screen	none	4 cm ² Teflon bonded $NiCo_2O_4$ on nickel screen (O_2 evolving)	45.60	45.60	49.82 \pm 1.11 (3)	1.34	5.41
D	25° C.	4 cm ² Teflon bonded Platinum black on	none	4 cm ² Teflon bonded $NiCo_2O_4$ on nickel (O_2 evolving)	N/A	45.60	46.96 \pm 0.68 (5)	1.26	5.36

TABLE 2-continued

Extraction of oxygen from air (400 mA passed through cell for 30 min)									
Cell No.	Temp.	Cathode	H ₂ O ₂ decomposer	Anode	Theoretical		Experimental ml (NTP)	Voltage iR free volt	Power consumption KW hr/1000 liters of O ₂
					From H ₂ O ₂ decomposition ml (NTP)	From O ₂ evolution ml (NTP)			
E	25° C.	Pt screen (O ₂ reduction) 4 cm ² Teflon bonded Platinum black on Pt screen	4 cm ² NiCo ₂ O ₄ on nickel screen	screen (O ₂ evolving) 4 cm ² Teflon bonded NiCo ₂ O ₄ on nickel screen	N/A	45.60	47.77	1.26	5.26
F	25° C.	Pt screen (O ₂ reduction) 4 cm ² Teflon bonded Pt black on Pt screen (H ₂ evolving)	none	screen (O ₂ evolving) 4 cm ² Teflon bonded NiCo ₂ O ₄ on nickel screen	N/A	45.60	45.80	2.09	9.12
G	40° C.	Teflon bonded Pt electrode (O ₂ reduction)	none	Teflon bonded Pt electrode (O ₂ evolving)	N/A	45.60	45.60	1.0	4.38

EXAMPLE 3

The catalytic activity of NiCo₂O₄ and CoFe₂O₄ catalytic decomposers was measured by a conventional gasometric technique.

In all cases the reaction rate constant was found to be independent of the initial H₂O₂ concentration but directly proportional to the catalyst mass, indicating first order Kinetics.

Experiments were conducted at 25° C., 30° C., 35° C. and 40° C. By plotting the first order reaction rate constant against the reciprocal of the temperature (degree kelvin) the activation energy for the decomposition of H₂O₂ over freeze dried NiCo₂O₄ (surface area 69.7 m²/g) was calculated as 10.98 Kcal/mole, similar to the value of 10.60 Kcal/mole obtained for CoFe₂O₄ (prepared by coprecipitation of cobalt and iron hydroxides followed by dehydroxylation at 100° C.) having a surface area of 120 m²/g.

Taking differences in surface area into account this shows the activity of NiCo₂O₄ to be approximately equivalent to that of CoFe₂O₄. However, NiCo₂O₄ is easier to prepare and apply to a screen and is thus currently preferred for use in the present invention.

It will be apparent from the above description that the present invention is especially advantageous in that it provides an oxygen generator which is highly efficient, which has a lower power consumption than hitherto proposed cells and which can be constructed from relatively cheap materials. It will be understood, however, that the electrochemical/chemical process described is not limited to such an application and other applications, modifications and variations falling within the scope of the present invention will be apparent to those skilled in the art.

We claim:

1. Oxygen extraction apparatus comprising at least one cell including a cathode for the reduction of oxygen by an electrochemical reaction thereby to produce peroxy ions, an anode adapted to regenerate oxygen, and said cell including, spaced apart from the cathode, means, other than the anode, for the catalytic decomposition of said peroxy ions.

2. Oxygen extraction apparatus comprising at least one cell including a cathode for the reduction of oxygen by an electrochemical reaction thereby to produce

peroxy ions, an anode adapted to regenerate oxygen, means for effecting catalytic decomposition of said peroxy ions to yield oxygen, said catalytic decomposition means being spaced apart from the cathode and not being electrically connected to either the cathode or anode.

3. Oxygen extraction apparatus as claimed in either claim 1 or 2 which comprises from 10 to 20 of said cells.

4. Oxygen extraction apparatus as claimed in either claim 1 or 2 wherein said cathode comprises a high surface area graphite powder.

5. Oxygen extraction apparatus as claimed in claim 4, wherein the powder has a surface area in the range of from 500 to 600 m²/g.

6. Oxygen extraction apparatus as claimed in claim 4, wherein the cathode is made from said graphite powder by bonding with polytetrafluoroethylene.

7. Oxygen extraction apparatus as claimed in either claim 1 or 2 wherein the means for the catalytic decomposition of peroxy ions comprises CoFe₂O₄ or NiCo₂O₄.

8. Oxygen extraction apparatus as claimed in claim 7, wherein the CoFe₂O₄ or NiCo₂O₄ is coated on a porous or perforated support.

9. Oxygen extraction apparatus as claimed in claim 8, wherein said support is a nickel screen.

10. Oxygen extraction apparatus as claimed in claim 7, wherein the CoFe₂O₄ or NiCo₂O₄ is bonded with polytetrafluoroethylene.

11. Oxygen extraction apparatus as claimed in either claim 1 or 2 wherein the means for the catalytic decomposition of peroxy ions comprises a spinel oxide or silver.

12. Oxygen extraction apparatus as claimed in claim 11, wherein the spinel oxide or silver is coated or absorbed on a graphite or carbon support.

13. Oxygen extraction apparatus as claimed in either claim 1 or 2 which comprises means for supplying ambient air to the cell at a suitable rate.

14. Oxygen extraction apparatus as claimed in either claim 1 or 2 which comprises means for collecting the oxygen produced by the electrochemical and catalytic reactions.

15. Oxygen extraction apparatus as claimed in claim 14, which comprises means for removing electrolyte entrained in the oxygen product stream.

16. Oxygen extraction apparatus as claimed in claim 14, which is provided with means for controlling the oxygen content of the final outlet gas by incorporating

exhaust gas from the cathode compartment with the oxygen product stream.

17. Oxygen extraction apparatus as claimed in either claim 1 or 2 wherein there is a porous screen between the cathode and the remainder of the cell.

18. Oxygen extraction apparatus as claimed in claim 17, wherein said porous screen is made from asbestos or glass.

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